

A Multi-Compound Model for the Hydration of Portland Cement – Fly Ash Binders

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ABSTRACT

In this study traditional reaction equations (based on the theory of Powers) are applied on the hydration reactions of Portland cement and the pozzolanic reaction of fly ash separately. Moreover, Portland clinker is considered as a mixture of four minerals each with their own sensitivity to the presence of fly ash. The kinetics of the reactions of each clinker mineral have been analysed by fitting generally known models such as the Avrami and Jander equations to isothermal heat measurements on pastes of cement, fly ash and water. The proposed model therefore consists of different stages, in which nucleation, phase-boundary and diffusion reactions, become rate-controlling. The kinetics of the pozzolanic reactions have been described with similar equations, implementing parameter values based on measured selective dissolution data. Fly ash may accelerate the reaction of a clinker mineral, while at the same time it can decelerate another mineral.

INTRODUCTION

A more intensive application of industrial by-products with pozzolanic or cementitious characteristics in concrete mixtures can contribute to a reduced emission of carbon dioxide, and a saving of natural resources. Although the use of fly ash has significantly increased over the years, it still remains unclear how its influence can be implemented correctly in a civil engineering design. Due to the uncertainty concerning the cement and fly ash interaction, the European code EN 206-1 applies the more pragmatic k-value approach. However, this approach remains inadequate to explain the durability and microstructural behaviour of concrete with fly ash. Moreover, it cannot offer an answer on whether the presence of fly ash has an accelerating or decelerating effect on the cement hydration.

MATERIALS AND METHODS

Characterization of materials and mixtures

Ordinary Portland cement CEM I 51.5 N, complying with European Standard EN 197-1 (2000) is used in all paste mixtures as hydraulic binder. Table 1 lists the chemical composition of the Portland cement considered, according to the EN 196-2 (2005). The theoretical mineralogical composition of the clinker, derived from the chemical analysis using the Bogue calculation is also given. The difference between the different cements used

in this study, is mainly the different contents of C₂S, C₃A and C₄AF. The amount of C₃S remains rather constant.

Low calcium fly ashes (named respectively FA(1), FA(2), FA(3), FA(4) and FA(5)) from West European origin are used as partial cement replacement material in the fly ash-cement pastes. Table 2 lists the chemical compositions of the studied fly ashes according to EN 196-2.2 (2005) with the loss on ignition (LOI), glass fraction according to CUAP “Fly Ash for Concrete” (annexe B) (2006) (ETA request No. 0301/34) and fineness according to NBN EN 451-2 (1995). In the latter reference, the fineness is defined as the fraction which is retained on a sieve of 0.045 mm during a wet sieving test.

Each paste mixture is given a typical name, which consists of three codes. The first code C indicates the cement type according to Table 1, followed by the percentage of cement-to-cementitious material. The second code defines the type of fly ash according to Table 2, which was used in the binder as (partial) cement replacer, followed by the percentage of fly ash-to-cementitious material. The final code W is followed by the percentage water-to-cementitious material.

Table 1. Characterization of the Different Cements

Code	C(I) CEMI52.5 N	C(II) CEMI52.5 N	C(III) CEMI52.NHSRLA
Analysis of oxides			
SiO ₂ (%)	19.60	18.27	19.94
Al ₂ O ₃ (%)	4.90	5.61	3.13
Fe ₂ O ₃ (%)	3.10	4.39	4.76
CaO (%)	63.60	62.60	61.56
MgO (%)	0.90	0.85	--
K ₂ O (%)	0.77	0.95	0.66
Na ₂ O (%)	0.41	0.53	0.24
SO ₃ (%)	3.30	2.40	2.54
LOI (%)	2.10	0.90	5.45
Constituents based on Bogue calculations			
C ₃ S (%)	63.19	65.2	63.93
C ₂ S (%)	8.50	3.30	9.03
C ₃ A (%)	7.70	7.40	0.25
C ₄ AF (%)	9.70	13.30	14.47
Blaine fineness(m ² /kg)	360	480	310

Table 2: Characterization of the Different Fly Ashes

Code	FA(1)	FA(2)	FA(3)	FA(4)	FA(5)
Analysis of oxides					
SiO ₂ (%)	53.31	53.06	53.84	49.34	59.98
Al ₂ O ₃ (%)	26.43	23.96	26.55	24.55	23.28
Fe ₂ O ₃ (%)	7.53	6.50	6.48	6.23	4.94

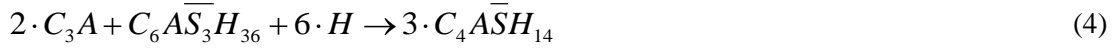
CaO (%)	4.46	2.51	1.96	2.47	4.8
MgO (%)	2.45	1.79	1.70	1.73	0.58
K ₂ O (%)	3.58	3.32	4.48	3.84	0.63
Na ₂ O (%)	1.15	1.08	0.52	0.51	0.24
SO ₃ (%)	0.90	0.86	1.00	0.30	n.a.
LOI (%)	4.10	3.53	3.90	5.24	5.4
Fineness (%)	24.0	24.4	22.4	38.5	13.8
Glass fraction (%)	n.a.	n.a.	67.75	62.75	51.37

Isothermal calorimetry. The reaction kinetics are measured by means of isothermal calorimetry performed on different fly ash – cement binders. Immediately after manual mixing of the cement and fly ash with water, 14 grams of each binder paste were placed in a calorimeter to measure isothermally the exothermal hydration process. This test was performed for each binder mixture three times for different isothermal conditions varying between 10°C and 60°C. At 10°C, the calorimeter was flushed with dry air to prevent condensation. The heat evolved per time unit was monitored and recorded at constant time intervals.

A MULTI-COMPOUND MODEL FOR FLY ASH – CEMENT KINETICS

Theoretical approach. The hydration of Portland cement is an exothermic and heterogeneous process. In order to physico-chemically describe the hydration process, at least a hybrid kinetic model is needed. This kind of model allows the state of the water, chemical composition of the cement and particle size distribution to play an explicit role in the rate of the reaction [Van Breugel 1991]. A clear insight in the different physical process which take place simultaneously during hydration, can only be studied by considering Portland as multi-mineral compound. In the following model, only the main four minerals are considered: alite, belite, calcium aluminate and ferrite. The hydration of alite is noticeable during the acceleration period of a isothermal heat release curve, while the hydration of belite mainly takes places during the final period. The stoichiometry of the corresponding reaction is given in equation (1) and (2). The hydration of calcium aluminate consists of ettringite formation from the reaction with anhydrite (or gypsum) (equation 3) and later on a conversion reaction of the ettringite with the unreacted fraction of calcium aluminate phase (equation 4). This conversion reaction can already take place before all sulphate is consumed [D'Aloia and Chanvillard 2002]. The reaction degree of the calcium aluminate phase at which the latter conversion reaction starts is called hereafter ‘ $\alpha_{\text{Al}_3\text{AF}_m}$ ’ [Baert 2009]. The stoichiometry can vary for these equations and mainly depends on the saturation level of the environment [Baert 2009]. Fully saturated conditions have been assumed in this study [Baert 2009]. Equation (4) represents the hydration of the ferrite phase. Other and complimentary equations have been proposed for the ferrite hydration [Brouwers 2005], but equation (4) is well-known and -used [Tennis and Jennings 2000]. A good correlation with modelled water retention has also been found [Baert 2009]. Along with the reactions of equation (1) to (5), heat is released: respectively 500 J/g_{alite}, 260 J/g_{belite}, 1670 J/g (C₃A to AF₁), 1140 J/g (C₃A to AF_m) and 420 J/g_{ferrite}.





The chosen stoichiometric equations describing the pozzolanic reaction in this study are equations (6), (7) and (8). These are based on equations proposed by Jiang et al. 2000, Bentz and Remond 1997, Helmuth 1987, Young and Hanssen 1987 and Brouwers [Brouwers and Van Eijk 2002]. Two reaction products are considered: pozzolanic calcium silicate hydrates (equation 7) and strätlingite (equation 8). Also some gypsum can be formed upon contact with water (equation 6). Only few data is available concerning the corresponding heat release of these reactions [Maekawa 1999; Schindler and Folliard 2003]. This parameter is also taken as unknown in the least squares analysis.



The heat rate can be divided in several stages: an initial peak, acceleration period, deceleration and final period. The model, presented hereafter, only considers the heat release from the acceleration period onwards. Herein, it is assumed that the reaction kinetics of cement is the sum of the heat rate of all cement minerals (equation (9)). Each heat rate consists of two material functions (equation (9)): a reference rate $f_i(\alpha_i)$, expressed per degree of hydration of mineral i and a second material function $g_i(\theta)$ expressed in function of the curing temperature θ . The degree of hydration of each clinker phase α_i at time step t (expressed in days) can be given numerically by equation (10).

$$\frac{d\alpha}{dt}(\theta) = \sum_i \frac{d\alpha_i}{dt}(\theta) = \sum_i f_i(\alpha_i) \cdot g_i(\theta) \quad (9)$$

wherein α_i is the hydration degree of mineral i (equation (10)), f_i the reference heat rate of mineral i , $g_i(\theta)$ the material function describing the sensitivity of the hydration of mineral i to the temperature θ , i can stand for either alite, belite, the aluminate phase or the ferrite phase.

$$\alpha_i(t) = \alpha_i(t - \Delta t) + \frac{d\alpha_i}{dt}(t) \cdot \Delta t \quad (10)$$

It is assumed that the hydration of the four clinker minerals takes place through three basic processes: dissolution/nucleation/growth, interaction at the boundaries and diffusion. The first process can be described by an overall kinetic equation (Avrami equations (11) and (12)). The second and third processes are described with particle kinetics: at the phase boundaries (equations (13) and (14)) and diffusion through the grains (Jander equations (15) and (16)). These three processes are assumed to take place simultaneously for each clinker mineral, but the slowest one will be the rate-controlling process. This principle has roughly earlier been proposed by Parrot and Killoh [Parrot and Killoh 1984]. Their findings are still used by Lothenbach in the thermodynamic approach [Lothenbach and Winnefeld 2006]. A similar principle has also been proposed by other investigators [Krstulovic and Dabic 2000].

$$\alpha_i = 1 - \exp\left[-k_{i-1}(t - t_0)^{\overline{n}_i}\right] \quad (11)$$

$$\frac{d\alpha_i}{dt} = K_{i-1} \cdot n_i \cdot (1 - \alpha_i)^{n_i} \ln(1 - \alpha_i)^{\frac{n_i-1}{n_i}} \quad (12)$$

$$\alpha_i = 1 - (1 - K_{i-2} \cdot (t - t_0)^3)^{\frac{1}{3}} \quad (13)$$

$$\frac{d\alpha_i}{dt} = 3 \cdot K_{i-2} \cdot (1 - \alpha_i)^{\frac{2}{3}} \quad (14)$$

$$\left[1 - (1 - \alpha_i)^{\frac{1}{3}}\right]^2 = K_{i-3} \cdot (t - t_0) \quad (15)$$

$$\frac{d\alpha_i}{dt} = \frac{3}{2} \cdot K_{i-3} \cdot \frac{(1 - \alpha_i)^{\frac{2}{3}}}{\left[1 - (1 - \alpha_i)^{\frac{1}{3}}\right]} \quad (16)$$

With K_{i-j} the rate constant, n_i the Avrami exponent describing crystal growth (ranging from 1 to 3), and t_0 the induction time.

The influence of water availability has also taken into account in equation (17): when a critical degree of hydration $H_i(w/c)$ is exceeded, the rate of hydration is reduced with a factor $h_i(w/c)$, varying between 1 and 0.

$$h_i\left(\frac{w}{c}\right) = \left(1 + 3,333 \left(H_i \frac{w}{c} - \alpha_i(t - \Delta t)\right)\right)^4 \text{ for } \alpha_i > H_i \frac{w}{c} \text{ and } h_i\left(\frac{w}{c}\right) = 1 \text{ for } \alpha_i < H_i \frac{w}{c} \quad (17)$$

The temperature dependency of cement can vary in the model with the clinker minerals, each dominating the hydration process at different stages and with the control processes according to which the minerals react. In order to make a general prediction of the temperature dependency, a changing thermal activity of cement is taken into account by allowing each mineral i to exhibit a different thermal activity during each control process j of that mineral (equation (18))

$$g_i(\theta) = K_{i-j} \cdot \exp\left[-\frac{E_a(i,j)}{R} \cdot \left(\frac{1}{273+20} - \frac{1}{273+\theta}\right)\right] \quad (18)$$

where $E_a(i,j)/R$ is the thermal activity of mineral i during the control process j with E_a the apparent activation energy and i standing for either alite or belite or the aluminate phase or the ferrite phase and j standing for either nucleation and growth or phase-boundary reactions or diffusion.

The reaction kinetic of the pozzolanic reaction in this model has been described with two reaction rate processes: the Avrami equation (19) for nucleation and growth and the Jander equation (20) for diffusion processes. Selective dissolution experiments have shown that the reaction kinetics of the pozzolanic reaction can be divided into two periods [Termkhajornkit, Nawa et al. 2005; Baert 2009].

$$\left[\frac{d\alpha_i}{dt}\right]_1 = K_{i-1} \cdot n_i \cdot (1 - \alpha_i)^{n_i} \ln(1 - \alpha_i)^{\frac{n_i-1}{n_i}} \quad (19)$$

$$\left[\frac{d\alpha_i}{dt} \right]_3 = \frac{3}{2} \cdot K_{i-2} \cdot \frac{\left(-\alpha_i \left(-\Delta t \right)^{\frac{2}{3}} \right)}{\left[1 - \left(-\alpha_i \left(-\Delta t \right)^{\frac{1}{3}} \right) \right]} \quad (20)$$

At first the pozzolanic reaction is controlled by the Avrami equation, describing nucleation and growth on the surface particle of the fly ash. From a time, indicated as τ_{FA_D} , the process becomes diffusion-controlled and can be described by the Jander equation. The unknown parameters are K_{FA_1} , n_{FA} , τ_{FA_D} and K_{FA_2} . These coefficients are calculated from a least squares analysis with the reaction degrees of the fly ashes, measured with selective dissolution [Baert 2009]. Based on the simulations with the five fly ashes used in this study, it was found that the reactivity of fly ash in cement-fly ash pastes could be described with a fixed n_{FA} and K_{FA_2} , independent from the fly ash characteristics: 0.68 for n_{FA} and $8 \cdot 10^{-6}$ for K_{FA_2} [Baert 2009]. The time τ_{FA_D} seems to depend on the fly ash type, but not on the fly ash-binder ratio nor on the cement type.

Due to the presence of fly ash, the reaction kinetics of the Portland clinker minerals will change. To quantify this, the assumption has been made that if a particular fly ash influences the hydration of a clinker mineral of a Portland cement, it will also influence the hydration of the same clinker mineral of another Portland cement in the same way and magnitude: e.g. if fly ash FA(1) accelerates the ferrite fraction of C(I), it also necessarily accelerates the ferrite fraction of C(II) and C(III) in the same way and magnitude. Therefore the parameters K_{i-1} , n_i , K_{i-2} , K_{i-3} , H_i , E_{ij} of equations (12), (14) and (16) are calculated for pastes with a partial replacement of the cement content by a fly ash with equations (21) to (24).

$$K_{i-j}_{C+FA} = K_{i-j}_C + \frac{FA}{B} \cdot K_{i-j}_{FA} \quad (21)$$

$$n_{i}_{C+FA} = n_{i}_C + \frac{FA}{B} \cdot n_{i}_{FA} \quad (22)$$

$$H_{i}_{C+FA} = H_{i}_C + \frac{FA}{B} \cdot H_{i}_{FA} \quad (23)$$

$$E_{ij}_{C+FA} = E_{ij}_C + \frac{FA}{B} \cdot E_{ij}_{FA} \quad (24)$$

In these equations the symbol $(\dots)_{C+FA}$ stands for the parameter of a binder containing cement and fly ash, while symbol $(\dots)_C$ stands for the value of the parameters in plain Portland cement without any influence of supplementary cementitious materials $(\dots)_{FA}$ stands for the influence of a fly ash on the parameters (which is the same for all situations of that clinker mineral).

The effective water-cement ratio $(W/C)_{eff}$ is the mass ratio of water which participates in the hydration, to cement. The effective water-cement ratio is given in equation (27). The k-value is considered here as a fly ash characteristic. The amount of ettringite formed before the acceleration period is also considered to be a parameter in the model (α_{Aft}).

$$\left(\frac{W}{C} \right)_{eff} = \frac{W}{CM} \cdot \left(1 + k \cdot \frac{FA}{C} \right) \quad (27)$$

Practical approach. The hydration heat of each of the three ordinary Portland cements has been registered in an isothermal calorimeter at different curing temperatures (10°C, 20°C, 35°C, some at 18°C, 28°C, 60°C) and with water-cement ratios varying between 0.3 and 1.0. For each Portland cement, isothermal heat rates were available for an average of 4 curing temperatures and 4 water-cement ratios. One single least squares analysis has been performed for each Portland cement, taking all its measured data of the isothermal calorimetry into account. This yielded the parameters for each Portland cement. Isothermal heat calorimetry was performed for different cement-fly ash combinations. Again, for each fly ash one single least squares analysis is performed with all the available data of the isothermal calorimetry (all its combinations with ordinary Portland cements C(I), C(II) and C(III) at different curing temperatures and different water-binder ratios). This yielded the parameters for each fly ash.

APPLICATION OF THE KINETIC MODEL ON DIFFERENT FLY ASH – CEMENT COMBINATIONS

From the measured isothermal calorimetric curves, the model parameters and the hydration degrees of the clinker minerals and of the fly ashes can be found. The simulations for FA1 combined with C(I) in different ratios is shown in Fig.1. The heat rate of the fly ash is not plotted, since it is too low during the first seven days after mixing. The third hydration peak can be predicted with good accuracy. After performing the simulations, the influence of fly ash on the hydration degrees of cement and of its individual clinker minerals can be observed (**Error! Reference source not found.**-3). Fly ash FA(1) decelerates the alite hydration during the first day. However, afterwards in the diffusion period a higher hydration is obtained with increasing fly ash-binder ratio. A similar effect can be found for the ferrite hydration, however the change from a deceleration effect to an acceleration effect appears later in time with increasing fly ash content. Though a third hydration peak can be noticed when fly ash FA(1) partially replaces the cement content of C(I), the simulation indicates that the calcium aluminate hydration is decelerated with increasing fly ash content. The effect on the belite hydration can not be clearly given, since seven days of curing is a too short period to predict the belite hydration. With increasing fly ash content, the cement hydration (in its total) is enhanced (**Error! Reference source not found.**). The paste with a fly ash-binder ratio of 0.67 yields a significantly lower fly ash reaction compared to the other fly ash-cement pastes.

Not all fly ashes caused a third hydration peak in the cement hydration [Baert 2009]. The physico-chemical model, proposed here, can however be used to predict the heat rate for each of the studied fly ash-cement combinations. Although the shape of the heat rate of each combination can be totally different, **Error! Reference source not found.** shows that the interaction of fly ash with each clinker mineral is very similar for all fly ash - cement combinations. The alite experiences a deceleration followed by an acceleration. The hydration of calcium aluminate is almost for all fly ashes decelerated. Only fly ash FA(4) gives in the end a higher hydration degree of C_3A . Not all fly ashes cause an initial decrease in the ferrite hydration, but after one day they all enhance this hydration reaction. The magnitude of enhancement can however vary with the fly ash. Some fly ashes accelerate the belite hydration. For others, no clear conclusions concerning the belite reaction can be drawn. Almost all fly ashes cause a retardation of the initial total reaction degree. After 1 day however, all fly ashes start to enhance the cement reaction.

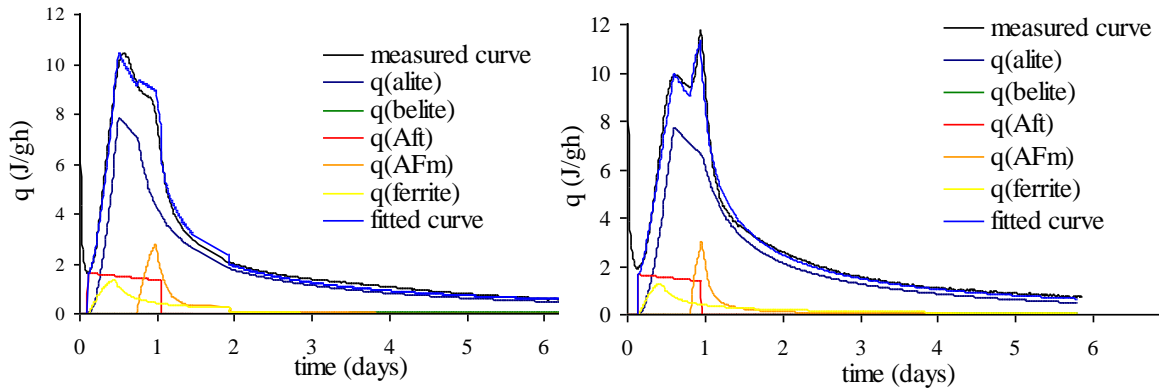


Fig. 1. Simulation of Heat Release at 20°C by the Cement Clinker Minerals of Cement C(I) and Fly Ash FA(1) in a Paste with Water-binder Ratio of 0.40 and Fly ash-binder Ratio of 0.35 (left), and 0.67 (right).

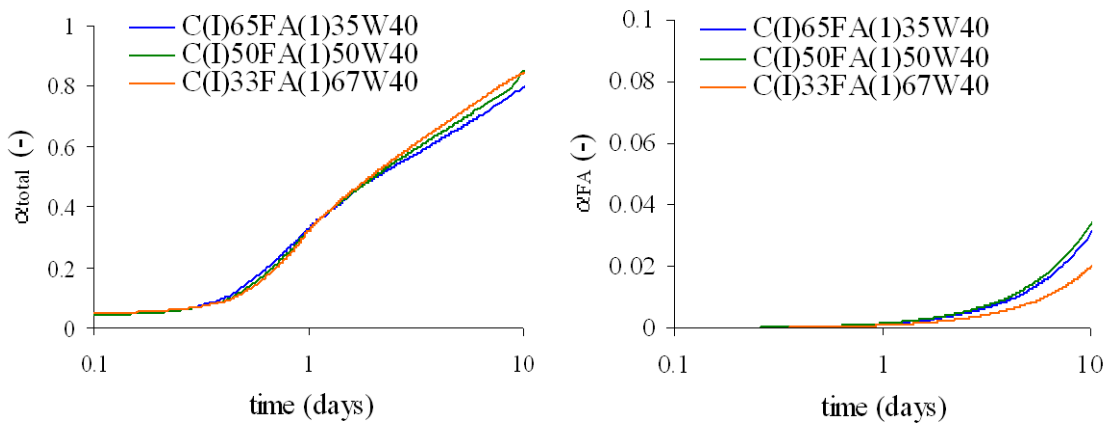


Fig. 2. Simulation of Hydration Degree at 20°C of Cement C(I) (left) and Reaction Degree of Fly Ash FA(1) (right) for Pastes with Different FA-binder Ratio

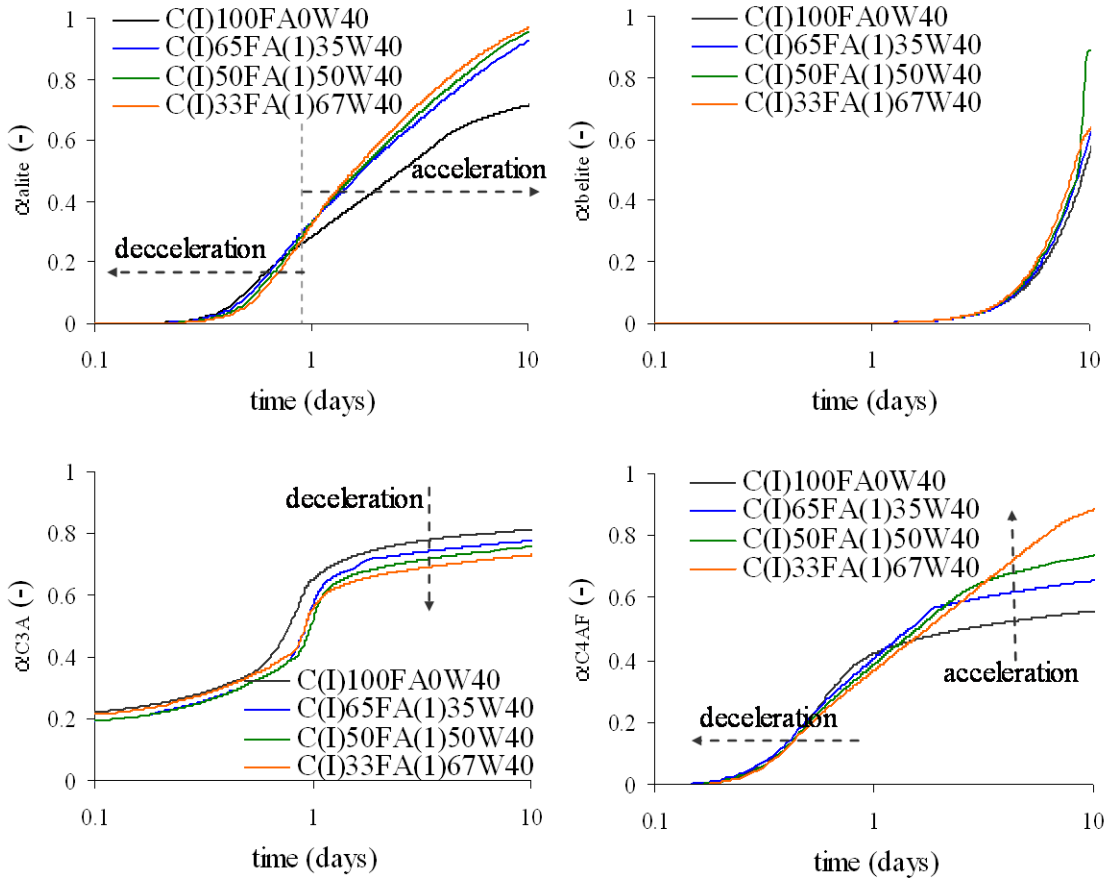


Fig. 3. Simulation of Hydration Degree of Clinker Minerals of Cement C(I) at 20°C for Pastes with FA(1) and Different FA-binder Ratio

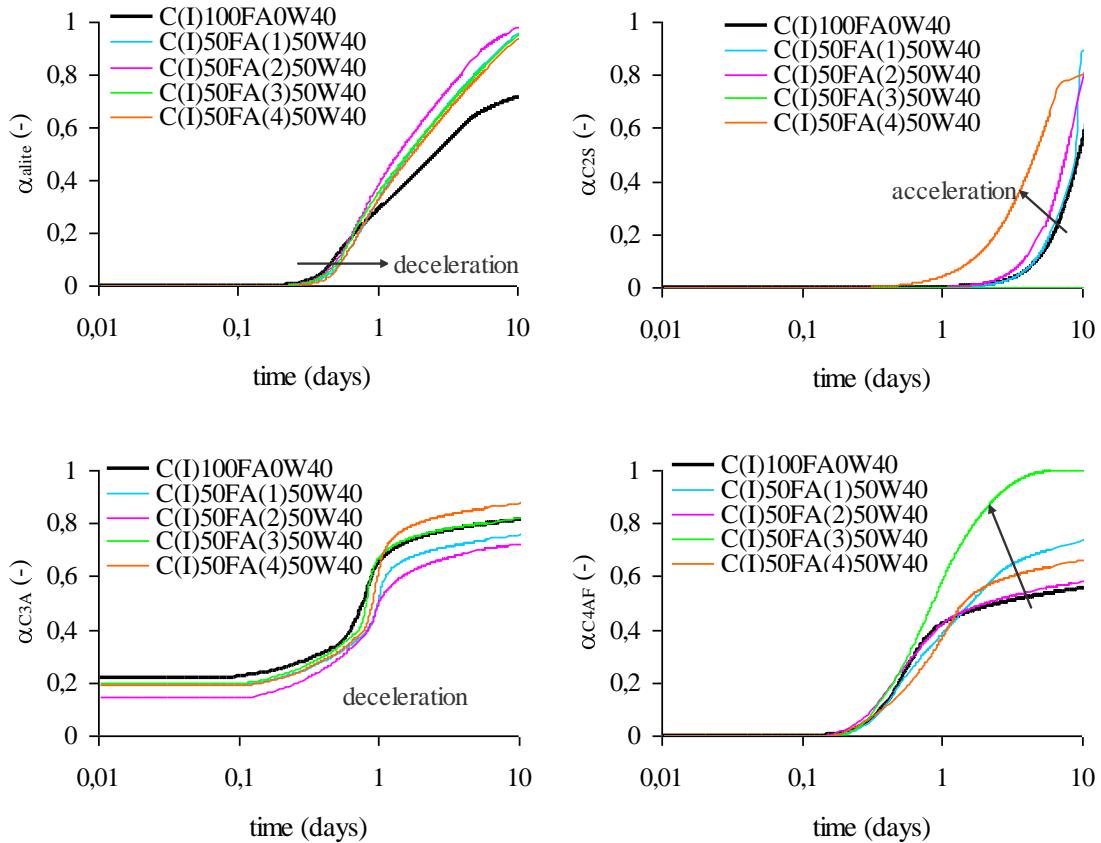


Fig. 4. Simulated Hydration Degree of the Clinker Minerals of Cement C(I) at 20°C in a Plain Portland Cement Paste and Paste with 50% Replacement of Cement by Fly ash FA(1), FA(2), FA(3) and FA(4), all with Water-binder Ratio of 0.40

CONCLUSIONS

A physico-chemical model has been built, which can indicate which mineral phases of Portland cement are enhanced or retarded through the presence of fly ash. Also, the reaction degree of fly ash can be determined in different situations (for different fly ash-binder ratios and different water-binder ratios). This model supports the “independent hydration” concept, rather than the “equal reaction rates” concept. The model uses equations which can be physically interpreted. Also the thermal activity has been modelled. The Arrhenius function has been used for the thermal sensitivity of the fly ash- cement interactions. This model can be used as an assessment tool for the interaction between ordinary Portland cement and fly ashes or other additions.

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